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Nonlinear optical studies of a fluorinated poled polyimide guest-host system

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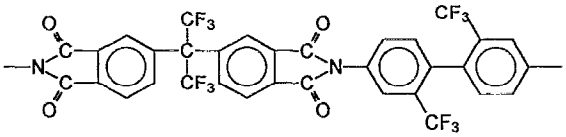
We report on poling of a low dielectric constant preimidized fluorinated fully aromatic guest-host polyimide nonlinear optical material including thermal stability of optical nonlinearities and waveguiding properties. We measured a second-harmonic coefficient (d_{33}=4.9±0.5 pm/V at 1217 nm fundamental wavelength) which is accurately predicted by a thermodynamic model of poled polymers. The optical nonlinearity of a poled sample was thermally stable at 80 °C for over 300 h. Films were observed to have negative birefringence. Optical losses for slab waveguides in lowest order TE and TM modes were ≥7.7 dB/cm for doped waveguides at 800 nm wavelength and increased after poling.

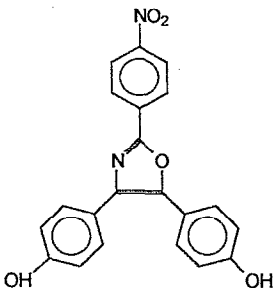
The nonlinear optical properties of poled polymeric materials have been researched recently.[1–5] The large optical nonlinearities of these materials gives them excellent potential for incorporation into nonlinear optical integrated devices. Such devices may need to operate for long periods of time at high temperatures (≈80 °C).[4] Poled polymer films such as Disperse Red-1 doped poly-(methylmethacrylate), will not retain their optical nonlinearities under such conditions due to their low glass-transition temperatures. Recently, the nonlinear optical properties of some novel high T_g poled polyimides have been investigated.[4,5] The high nonlinear optical susceptibilities of these materials have shown very good thermal stability when doped in a guest-host configuration. These systems, once cured and poled, have proven to be thermally stable for extended periods of time at elevated temperatures.[6]

Different methods have been explored for the curing and poling of polyimide guest-host systems. One method used a thermal process to imidize films during poling.[4,5] Room-temperature chemical imidization performed immediately after poling has been seen to enhance the thermal stability of the poled electro-optic response.[7] We report here on the nonlinear optical properties of a poled polyimide guest-host system that is soluble even after imidization. This allows films to be easily processed and poled fully imidized. The system is fully aromatic so its glass-transition temperature is very high. This feature is useful for device applications because it lessens the effects of relaxation after poling allowing the polyimide films to retain their second-order nonlinear optical properties for extended periods of time.

The polyimide we used was synthesized from 2,2′-bis(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA) and 2,2′-bis(trifluoromethyl)-4,4′-diaminobiphenyl (PFMB). The glass-transition temperature of the undoped polyimide is 357 °C as determined by dynamic mechanical strain analysis. This is much higher than the glass-transition temperature of the polyetherimide Ultem, which has been reported as 210 °C.[4] Very high temperatures were required to pole this polyimide so a nonlinear chromophore with very high decomposition temperature was necessary. Several molecules for such applications have been studied.[4,5,8] The dye we used was 2-(*p*-nitrophenyl)-4,5-bis(*p*-hydroxyphenyl) oxazole (TNON). The decomposition temperature of TNON is 305 °C and was measured by thermal gravimetric analysis. The chemical structures of TNON and 6FDA/PFMB are shown in Fig. 1, and Fig. 2 shows the glass-transition temperature of the guest-host system plotted as a function of dye content. Considerable plasticization by the chromophore was observed.



(a)



(b)

FIG. 1. The chemical structures of (a) 6FDA/PFMB and (b) TNON.

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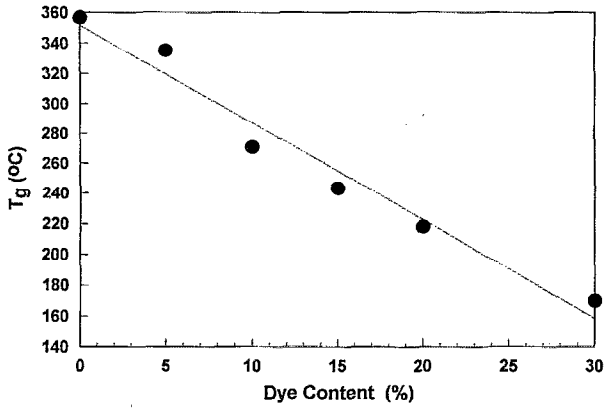

FIG. 2. Glass-transition temperature of the TNON-6FDA/PFMB guest-host system as a function of dye content determined by DMS. The line is a least-squares fit.

Films of TNON-6FDA/PFMB were spin coated onto indium-tin-oxide-coated glass and were then baked at 105 °C in a vacuum oven to remove excess solvent. After films were cast, they were corona poled in a nitrogen atmosphere with the field perpendicular to the film for 45 min at 300 °C. The poling field was approximated using an Isoprobe electrostatic voltmeter to measure the potential on the surface of the film with respect to ground.

Second-harmonic generation was measured by placing the film on a rotation stage in a 1217 nm laser beam. This wavelength and its second harmonic are both far from resonance of TNON-6FDA/PFMB. The absorption peak of the system is at 400 nm and was measured with a UV-vis spectrophotometer. The second harmonic produced by the film was then measured as a function of incident angle in both p and s polarizations. In both cases the second harmonic was p polarized. All measurements were referenced to d_{11} of quartz.

The second-order nonlinear optical susceptibility of the TNON-6FDA/PFMB films was calculated using rotational Maker fringe analysis.[9] Using a thermodynamic model, d_{33} for poled polymer films can be predicted using the molecular hyperpolarizability, β, of the chromophore[1]

$$d_{33}(-2\omega;\omega,\omega)=Nf^{2\omega}f^{\omega}f^{\omega}\beta_{zzz}(-2\omega;\omega,\omega)\left(\frac{p}{5}-\frac{p^3}{105}\right), \tag{1}$$

where

$$p=\left(\frac{\epsilon(n^2+2)}{n^2+2\epsilon}\right)\frac{\mu E_p}{kT}, \tag{2}$$

where N is the number density of nonlinear optical moieties, $f^{2\omega}$ and f^{ω} are the local field factors at the indicated frequencies, ϵ is the static dielectric constant, n the index of refraction, and E_p the poling field.

The value of β for TNON was measured by dc-induced second-harmonic generation while dissolved in 1,4-dioxane. The hyperpolarizability was calculated using an infinite dilution extrapolation procedure.[10] Table I shows several properties of the TNON-6FDA/PFMB films used for these experiments.

TABLE I. Physical parameters of TNON and 6FDA/PFMB used in calculations. ϵ is the static dielectric constant, E_p the magnitude of the poling field, n_ω the refractive index at the fundamental frequency, β the second order molecular nonlinear optical susceptibility, and μ the dipole moment. Both β and μ were measured by dc-induced second harmonic generation at λ=1344 nm.

Number density	ϵ	E_p (MV/cm)	n_ω	β (esu)	μ (esu)
5.703×10^{20}	2.8	2	1.57	3.6×10^{-29}	7.7×10^{-18}

The UV-vis spectrum of a TNON-6FDA/PFMB was measured for poled and unpoled films, and the height of the absorption peak at 400 nm decreased dramatically due to decomposition of the dye. The height of the absorption peak varies linearly with the number density of the film, and this decrease (of nearly 50%) was accounted for in the calculation with the thermodynamic model. This correction leads to excellent agreement between the measured nonlinear optical susceptibility and that predicted by the model as shown in Table II. This agreement along with the measured ratio $d_{33}/d_{31}=3.0\pm0.4$ indicates that poling of the guest-host polyimide system leads to the maximum attainable nonlinear optical coefficient in an isotropic poling regime.[9]

The induced alignment in these polyimide films was seen to have high thermal stability. The p-p experiment was repeated several times over a period of over 300 h with a poled film stored under ambient conditions at 80 °C. The signal showed some fast decay during the first few hours, but then stabilized as shown in Fig. 3. Another sample was stored for 30 min at 200 °C after poling, and d_{33} decreased by a factor of approximately 4. The thermal stability of the system could be further improved by chemically attaching the chromophore to the polymer main chain rather than doping in the guest-host configuration.

An equilateral prism coupling technique was used to locate radiation modes in TNON-6FDA/PFMB films cast on silicon. The indicent angles at which these modes were located were used to calculate the refractive indices in both TE and TM polarizations for wavelengths ranging from 514 to 800 nm. Figure 4 shows the dispersion in the refractive index of an unpoled film and a poled film. The birefringence was observed to be negative. The magnitude of the birefringence decreased during poling because of poling-induced order perpendicular to the plane of the film. The birefringence of about -0.02 for the poled films makes a negligible contri-

TABLE II. Comparison of the second order nonlinear optical susceptibility measured with Maker Fringes [d_{31} (measured) and d_{33} (measured)] and that predicted by the thermodynamic model based on the values of β and μ [d_{33} (predicted)]. Uncertainty in d_{33} (measured) reflects uncertainty in d_{31} (measured) which, in turn reflects uncertainty in the angles and amplitudes of the Maker Fringes. Uncertainty in d_{33} (predicted) is due to uncertainty in the number density.

d_{31} (measured) (pm/V)	d_{33} (measured) (pm/V)	d_{33} (predicted) (pm/V)
1.6±0.1	4.9±0.5	5.0±0.4

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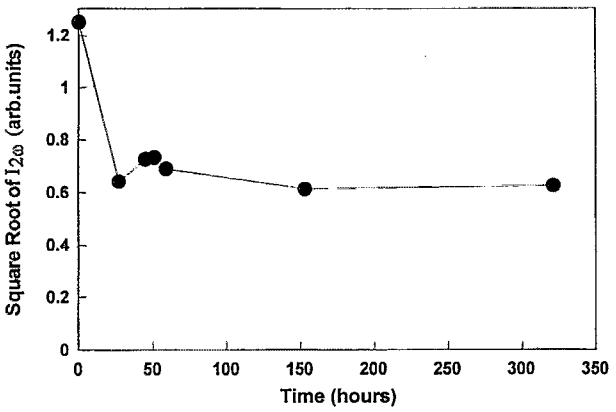

FIG. 3. The decay of the optical nonlinearity as a function of time after poling with the film stored at 80 °C.

bution in the calculation of the nonlinear optical susceptibility.[11]

A right angle prism coupler and scattered light imaging were used to measure the optical loss of slab waveguides cast on silicon dioxide. The incident angle of the laser was varied until the lowest order TE or TM mode would appear as a streak in the film, and the image of the streak was recorded by a Cortex frame grabber and digitized for data analysis. The optical loss was calculated using the assumption that the amount of light being guided inside the film was proportional to the amount of light scattered out of the film. Measured values of the loss are shown in Table III. Microscopic pinholes appeared on films during poling which caused large scattering losses.

The optical loss was measured in undoped and doped waveguides. The undoped samples showed markedly lower loss than the doped films at 800 nm. Loss measurements were repeated on the undoped films at 840 nm, and the loss was lower. These results indicate that the mechanism for the high loss seen in these polyimide waveguides is absorption

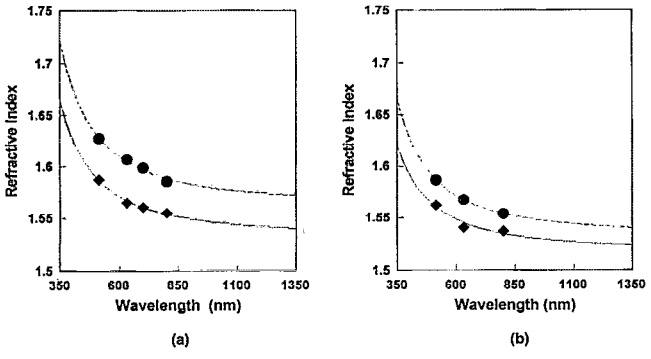

FIG. 4. Dispersion of the refractive index for 20% TNON-6FDA/PFMB films. Diamonds represent the TM indices, and circles show the TE indices—(a) is an unpoled film, and (b) is a poled film.

TABLE III. The optical loss of lowest order TE and TM modes of TNON-6FDA/PFMB slab waveguides.

	Wavelength (nm)	Loss of TE mode (dB/cm)	Loss of TM mode (dB/cm)
Undoped film	840	3.5	4.4
Undoped film	800	5.0	5.8
Doped unpoled film	800	8.2	7.7
Doped poled film	800	13.3	9.3

by both the chromophore and the polyimide host.[12,13] The loss could therefore be lowered by waveguiding at longer wavelengths which are farther from the absorption peak of the TNON-6FDA/PFMB system. Chemical modifications to lower the optical loss in polyimide waveguides are also possible and have been studied recently.[14]

The thermoplastic poling of a preimidized fluorinated fully aromatic polyimide guest-host system was observed to conform with a thermodynamic model based on noninteracting dipoles. This demonstrates that fully imidized soluble polyimide hosts can be effectively poled using standard techniques and opens new processing possibilities in the construction of polymer electro-optic devices. The aromaticity of the system gives it a high glass-transition temperature which minimizes relaxation at temperatures well above room temperature, and the exceptionally low dielectric constant suggests that very high bandwidth electro-optic devices may be constructed.

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